Reference (8)

DECLARATION

I, Maho KASEKI, c/o the Inoue & Associates of 3rd Floor, Akasaka Habitation Building, 3-5, Akasaka 1-chome, Minato-ku, Tokyo, Japan do solemnly and sincerely declare that I am conversant with the Japanese and English languages and that I have executed with the best of my ability this translation into English of Unexamined Japanese Patent Application Laid-Open Specification No. Sho 63-130644 and believe that the translation is true and correct.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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(Date)

Maho Kaseki
Maho KASEKI

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(72) Inventor: Takeo Sawanobori

c/o Research Institute, Mitsubishi Kasei Kogyo Co., Ltd.

1000 Kamoshida-cho, Midori-ku, Yokohama-shi, Kanagawa

(72) Inventor: Hideyuki Hisa

c/o Research Institute, Mitsubishi Kasei Kogyo Co., Ltd.

1000 Kamoshida-cho, Midori-ku, Yokohama-shi, Kanagawa

(72) Inventor: Kenichi Yoshie

c/o Research Institute, Mitsubishi Kasei Kogyo Co., Ltd.

1000 Kamoshida-cho, Midori-ku,
Yokohama-shi, Kanagawa
(72) Inventor: Yoshiteru Sakurazawa
c/o Research Institute, Mitsubishi Kasei Kogyo Co., Ltd.
1000 Kamoshida-cho, Midori-ku,
Yokohama-shi, Kanagawa
(71) Applicant: Mitsubishi Kasei Kogyo Co., Ltd.
5-2, Marunouchi 2-chome, Chiyoda-ku, Tokyo
(74) Agent: Hajime Hasegawa, patent attorney, and one else

SPECIFICATION

1. Title of the Invention

Electroconductive Film

2. Scope of Claims for Patent

(1) An electroconductive film obtained by a melt extrusion method, which comprises carbon black and a thermoplastic resin, wherein said carbon black is produced by the furnace process, and has a pore volume of 2.5 cc/g or less as measured by mercury porosimetry; a maximum peak of a pore distribution curve at 200 Å or more, said pore distribution curve being obtained by mercury porosimetry; and a dibutyl phthalate (DBP) oil absorption value of from 20 to 250 ml per 100

g of said carbon black.

(2) The electroconductive film according to claim 1, which has a thickness of 30 µm or less.

(3) The electroconductive film according to claim 1, wherein the amount of said carbon black is 20 to 200 parts by weight, relative to 100 parts by weight of said thermoplastic resin.

(4) The electroconductive film according to claim 1, wherein said thermoplastic resin is selected from the group consisting of polypropylene, nylon, polycarbonate and polyethylene terephthalate.

(5) The electroconductive film according to claim 1, wherein said carbon black has a pore volume of 2.5 cc/g or less as measured by mercury porosimetry; a maximum peak of a pore distribution curve at 300 Å or more, said pore distribution curve being obtained by mercury porosimetry; and a dibutyl phthalate (DBP) oil absorption value of from 20 to 250 ml per 100 g of said carbon black.

3. Detailed Description of the Invention

[Application Field in Industry]

The present invention relates to an electroconductive film. More particularly, the present invention is concerned with an electroconductive film which can be advantageously used as an electrosensitive transfer recording material for obtaining a printed record in the field of a noiseless typewriter, a computer or a facsimile; a material for a jacket of a floppy disk or compact disk; and a material for a container used for the storage and transport of an IC or LSI.

[Prior Art]

In recent years, in the field of a computer, a facsimile or the like, attention has been drawn to a thermal transfer printing method, since this method is nonimpact, noiseless and inexpensive and enables the size reduction and weight reduction of a printer. Especially, a thermal transfer printing method using a resistive ribbon thermal print head is regarded as the most prospective method for obtaining a useful hard copy.

Generally, a printing method using electrosensitive transfer recording is performed as follows. A resistive ribbon thermal print head comprising a front electrode (i.e., printing electrode) and a back electrode is impressed on an electrosensitive transfer recording material comprising a re-

sistive layer, a conductive layer and an ink layer, thereby conducting electricity through the electrosensitive transfer recording material. By the electricity conducted through the electrosensitive transfer recording material, heat is generated from the resistive layer of the electrosensitive transfer recording material, thereby increasing the temperature of the resistive layer. The heat generated from the resistive layer is transferred through the conductive layer to the ink layer, thereby heating the ink layer. By the heating of the ink layer, the ink contained in the ink layer is melted. The melted ink flows and is transferred to the recording material as a transferred record.

In the electrosensitive transfer recording method, the resistive layer is caused to generate heat due to the electricity conducted therethrough. Therefore, it is important to appropriately adjust the resistance of the resistive layer. With respect to the production of a resistive layer having an appropriate resistance, there have conventionally been known various methods, such as a method in which a dispersion of a metal powder (such as a copper powder, an iron powder or an aluminum powder) in a resin is shaped into a resistive layer in the form of a sheet or film (hereinafter referred to simply as a "resistive layer"); a method in which a dispersion

of graphite or acetylene black in a resin is shaped into a resistive layer (see Examined Japanese Patent Application Publication No. Sho 56-27382); a method in which a dispersion of carbon black in a resin solution, wherein the carbon black has a DBP oil absorption value of at least 300 ml per 100 g of the carbon black, is shaped into a resistive layer by a solvent casting method (see Unexamined Japanese Patent Application Laid-Open Specification No. Sho 60-71293); and a method in which a dispersion of carbon black in a resin is shaped into a resistive layer by a melt extrusion method (see Unexamined Japanese Patent Application Laid-Open Specification No. Sho 59-120494).

[Problems to Be Solved by the Invention]

However, the productions of resistive layers by the above-mentioned conventional methods have problems. For example, when a resistive layer is produced by the method using a dispersion of a metal powder in a resin, it is difficult to disperse the metal powder uniformly in the resin and, hence, the printing performance of a printing material using the resistive layer is lowered. On the other hand, when a resistive layer is produced by the method using a dispersion of graphite or acetylene black in a resin, it is difficult to obtain a resistive layer having a surface resistance

sufficiently small for practical use. Further, when a resistive layer is produced by the solvent casting method using a dispersion of carbon black (having a DBP oil absorption value of at least 300 ml per 100 g of the carbon black) in a resin solution, it is possible to obtain a resistive layer having a satisfactorily small surface resistance, but the solvent casting method is disadvantageous in that the method requires the use of complicated apparatuses for the application of the resin solution onto a substrate and the drying and recovery of a solvent. Furthermore, when a resistive layer is produced by the melt extrusion method, disadvantages are caused not only in that the produced resistive layer exhibits a very large surface resistance and a very large specific resistance, thus requiring a high voltage, but also in that the moldability is unsatisfactory. As seen from the above, the above-mentioned methods are not practicable. Thus, it has been desired to develop an electroconductive film exhibiting excellent moldability and a low resistance.

[Means to Solve the Problems]

In this situation, the present inventors have made extensive and intensive studies with a view toward solving the above-mentioned problems accompanying the prior art. In their studies, they have focused on the production of an

electroconductive film by the melt extrusion method using simple apparatuses. As a result, it has unexpectedly been found that an electroconductive film exhibiting satisfactorily low surface and specific resistances and exhibiting excellent moldability can be obtained by the use of a specific carbon black produced by the furnace process, wherein the carbon black is used for imparting electroconductivity to a film. Based on this finding, the present invention has been completed.

That is, it is an object of the present invention to provide an electroconductive film exhibiting excellent properties, which functions at low voltages and can be advantageously used as a high performance electrosensitive transfer recording material having excellent durability. This object can be easily attained by an electroconductive film obtained by a melt extrusion method, which comprises carbon black and a thermoplastic resin, wherein the carbon black is produced by the furnace process, and has a pore volume of 2.5 cc/g or less as measured by mercury porosimetry; a maximum peak of a pore distribution curve at 200 Å or more, the pore distribution curve being obtained by mercury porosimetry; and a dibutyl phthalate (DBP) oil absorption value of from 20 to 250 ml per 100 g of the carbon black.

Hereinbelow, the present invention is described in detail.

The carbon black used in the electroconductive film of the present invention is produced by the furnace process and has a pore volume of 2.5 cc/g or less as measured by mercury porosimetry; a maximum peak of a pore distribution curve at 200 Å or more, preferably 300 Å or more, the pore distribution curve being obtained by mercury porosimetry; and a dibutyl phthalate (DBP) oil absorption value of from 20 to 250 ml per 100 g of the carbon black.

Specific examples of carbon blacks include furnace carbon blacks "E-UHS", "#30B", "APF", "#10B" and "#5B" (each manufactured and sold by Mitsubishi Kasei Kogyo Co., Ltd.). With respect to the type of the thermoplastic resin used in the electroconductive film of the present invention, there is no particular limitation so long as the thermoplastic resin is one which is conventionally used in the field of information technology, such as a thermal transfer printer. Preferred examples of thermoplastic resins include polyethylene terephthalate, polystyrene, polyvinyl chloride, polycarbonate, nylon, polyethylene and polypropylene. Of these thermoplastic resins, nylon, polypropylene, polycarbonate and polyethylene terephthalate are especially preferred from the view-

point of obtaining an electroconductive film exhibiting excellent thermal resistance and durability.

In the electroconductive film of the present invention, the amount of the carbon black is from 20 to 200 parts by weight, preferably from 30 to 150 parts by weight, relative to 100 parts by weight of the thermoplastic resin. If desired, the electroconductive film of the present invention may further contain an appropriate amount of at least one additive selected from the group consisting of a dispersant, a softening agent and a lubricant.

The electroconductive film of the present invention is produced by a process in which the carbon black and the thermoplastic resin are uniformly mixed while heating, and the resultant mixture is shaped into a film having a thickness of 30 μm or less by a melt extrusion method.

With respect to the melt extrusion method, there is no particular limitation, and any conventional method can be employed. Specific examples of melt extrusion methods include a method (T-die method) in which a flat film is obtained by extrusion using a T-die, and a method (inflation method) in which a homogeneous mixture of the carbon black and the thermoplastic resin is extruded through a ring-shaped, round die while blowing thereinto a compressed gas, thereby forming a

tubular film. The film obtained by any one of the above-mentioned methods may be stretched.

The thus obtained electroconductive film of the present invention can be used in various application fields. Especially, the electroconductive film can be advantageously used as a resistive layer for an electrosensitive transfer recording material having a laminate structure comprising a resistive layer, a conductive layer and an ink layer or comprising a resistive layer, a conductive layer, a release layer and an ink layer.

For example, when it is intended to produce an electrosensitive transfer recording material having a laminate structure comprising a resistive layer, a conductive layer and an ink layer, the production thereof is performed as follows. First, a resistive layer comprising the electroconductive film of the present invention is produced by any one of the above-mentioned methods. Next, a thin film (such as a thin film made of aluminum) having excellent electroconductivity is formed as a conductive layer on the resistive layer by a conventional method, such as a deposition method. Subsequently, an ink layer is formed on the conductive layer (which has been formed on the resistive layer) by a hot-melt coating method or a solution coating method, thereby obtain-

ing an electrosensitive transfer recording material comprising a resistive layer, a conductive layer and an ink layer.

With respect to the ink layer, there is no particular limitation so long as the ink layer can be used in a conventional thermal transfer recording material. As a preferred example of the ink layer, there can be mentioned an ink layer comprising about 60 % by weight of a wax, such as a paraffin wax, a modified wax or a carnauba wax; about 20 % by weight of a pigment or dye; and about 20 % by weight of a resin.

The ink layer, the conductive layer and the resistive layer are formed by the above-mentioned method. It is preferred that the thicknesses of the ink layer, conductive layer and resistive layer are, respectively, from 1 to 10 μm, from 0.01 to 0.2 μm, and 30 μm or less; more advantageously from 2 to 5 μm, from 0.05 to 0.1 μm, and 20 μm or less.

If desired, from the viewpoint of easy separation between the ink layer and the conductive layer, a release layer made of polyketone or the like may be interposed between the ink layer and the conductive layer.

[Examples]

Hereinbelow, the present invention will be described in more detail with reference to the following Examples, Comparative examples and Reference Example, which should not

be construed as limiting the scope of the present invention.

Example 1

1.4 kg of polypropylene (Novatec P-4100Y; manufactured and sold by Mitsubishi Kasei Kogyo Co., Ltd.; MI: 1.2 g/10 minutes) and 0.6 kg of carbon black having properties as shown in Table 2 were charged into a Henschel mixer having an inner volume of about 9 liters, and the contents of the mixer were mixed at a rate of 2,500 rpm at room temperature for 1 minute.

The resultant mixture was placed in a vacuum dryer heated at 120 °C and dried for 12 hours, followed by a kneading using a twin-screw extruder, to thereby obtain a compound in the form of pellets. The obtained compound was dried using the vacuum dryer at 120 °C for 24 hours, and the resultant, dried compound was shaped into a film by using a single screw extruder (30 ϕ, 4D = 22) under conditions as shown in Table 1 below, thereby obtaining an electroconductive film. Various properties of the obtained electroconductive film are shown in Table 1.

Examples 2 to 4 and Comparative Examples 1 to 3

An electroconductive film was produced in substantially the same manner as in Example 1, except that the amounts of the polypropylene and carbon black charged into the Henschel

mixer and the type of carbon black were changed as shown in Table 1 below. Various properties of the carbon blacks used in these Examples and Comparative Examples are shown in Table 2 below.

Reference Example

Using a commercially available vacuum deposition device, an aluminum layer having a thickness of 0.08 μm was formed on the electroconductive film obtained in Example 1.

Subsequently, an ink having the below-mentioned composition was applied onto the surface of the above-obtained aluminum layer, so that an ink layer having a thickness of 4 μm was formed on the aluminum layer.

The composition and method for producing the ink:

Carbon black: 15 parts

(MA-8; manufactured and sold by Mitsubishi Kasei Kogyo Co., Ltd.)

Paraffin wax: 25 parts

Oxidized wax: 40 parts

Ethylene/vinyl acetate copolymer: 20 parts

(TM-PEV-720; manufactured and sold by Hoechst AG)

The above-mentioned components were mixed together using a mixer, and the resultant mixture was preliminarily kneaded, followed by kneading for five times using a three-roll mill,

wherein each of the rolls had a length of 6 inches, thereby obtaining an ink (ribbon). In the thus obtained ink, no agglomerated particles of carbon black having a size of 3 μm or more were observed. Using the ribbon, a printing was performed on a piece of ordinary paper under conditions wherein the applied voltage was 12 V, the pulse frequency was 100 Hz, the pulse width was 2 ms and the feed rate was 16 mm/s. As a result, it was found that the printed characters were clear and free from defect.

It was also found that a printed matter obtained using the above-mentioned ribbon was superior to a printed matter obtained by using a commercially available ribbon for printing.

Further, it was also found that, by the use of the resistive layer comprising the electroconductive film having a resistance as small as about 10 ohms, it became possible to perform a printing at voltage as low as 12 V.

Evaluation of various properties

Various properties of carbon black were measured as follows. With respect to the DBP oil absorption value, the measurement was performed in accordance with JIS-K-6221-A.

With respect to each of the pore volume and the position of a maximum peak of the pore distribution curve, the meas-

urement thereof was performed by mercury porosimetry with respect to the pore diameters in the range of from 75 to 75,000 Å (the measurement was performed using a measuring device (Auto Pore-9200; manufactured and sold by Micromeritics Instrument Corporation)).

With respect to the MI of the compound, the measurement thereof was performed by extruding the compound using a melt indexer (manufactured and sold by Takara Kogyo Kabushiki Kaisha) at 230 °C under a load of 11 kg.

The resistance of the electroconductive film was measured using an apparatus as shown in Fig. 1.

Specifically, the measurement of the resistance of the electroconductive film was performed as follows. A film specimen (1) having a diameter of 30 mm or more was interposed between two electrodes (electrode (2): the upper electrode (1100 g); electrode (2″): the lower electrode), each having a diameter of 25 mm. 1.0 kg of a load (3) was put on the upper electrode (2). 30 seconds after the load was applied to the upper electrode (2), the resistance of the film specimen was measured using a resistance meter (4) (Digital multimeter TR-6856; manufactured and sold by Takeda Riken).

With respect to the moldability of an electroconductive

film, the evaluation thereof was performed as follows. Using a commercially available dial thickness meter (having the capability of measuring the thickness of an object having a thickness of 1 μm or more), the thickness of an electroconductive film obtained by T-die extrusion and having a thickness of 10 cm was measured at 30 or more different portions of the film. Based on the results of the measurement, the moldability of the film was evaluated by the following criteria:

○: the variation in thickness relative to the average thickness is 10 % or less.

△: the variation in thickness relative to the average thickness is from 10 to 20 %.

×: the variation in thickness relative to the average thickness is 20 % or more.

Table 1

		Examples				Comparative Examples		
		1	2	3	4	1	2	3
Material	Type of resin	"Novatec P-4100Y"				"Novatec P-4100Y"		
	Amount of resin (%)	70	70	70	60	82	82	70
	Type of carbon black	"E-UHS"			"#10B"	"#3950B"	"Ketjen black-EC"	"Conductex-SC"
	Amount of carbon black (%)	30	30	30	40	18	18	30
Conditions for the shaping of film	Die temperature (°C)	200	200	200	200	200	200	200
	Clearance of the lip (m/m)	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	Amount extruded (kg/HR)	1.6	1.6	3.2	1.6	1.4	1.4	1.6
	Haul-off speed (m/minute)	11.5	8.3	11.5	11.5	11.5	11.5	11.5
Properties of film	Film thickness (μ)	17	20	28	17	20	20	17
	Moldability	○	○	○	○	△	△	△
	Resistance (ohm)	8	13	18	5	60	54	75
MI of carbon black compound (g/10 minutes)		3.9	3.9	3.9	2.8	0.4	0.5	1.2

Table 2

	"#10B"	"E-UHS"	"#3950B"	"Ketjen black-EC"	"Conduc-tex-SC"
DBP (cc/100 g)	83	187	357	367	100
Pore volume (cc/g)	0.75	1.70	2.58	3.09	1.22
Position of a maximum peak in the pore distri-bution curve	600	580	No peak observed	no peak observed	167

Notes)

1) Carbon blacks "H10B", "E-UHS" and "#3950" are manufactured and sold by Mitsubishi Kasei Kogyo Co., Ltd.

2) Carbon black "Ketjen black-EC" is manufactured and sold by Lion Akzo Co., Ltd.

3) Carbon black "Conductex-SC" is manufactured and sold by Columbian Chemicals Company.

[Effect of the Invention]

By the present invention, it becomes possible to easily obtain an electroconductive film which has excellent mold-ability and can generate a satisfactory amount of heat even at low voltages. The electroconductive film of the present invention can be advantageously used especially as an elec-trosensitive transfer recording material which can be satis-factorily used at low voltages and which exhibits excellent durability.

4. Brief description of the drawing

Fig. 1 shows a resistance measuring apparatus used for measuring the resistance of the electroconductive film of the present invention.

1; film specimen,

2, 2″; electrode,

3; load, and

4; resistance meter.

Applicant: Mitsubishi Kasei Kogyo Co., Ltd.

Agent: Hajime Hasegawa, patent attorney, and one else